재 료 상 변 태

Phase Transformation of Materials

2008.09.30.

박 은 수

서울대학교 재료공학부

Contents for previous class

- **Ternary Equilibrium: Ternary Phase Diagram**

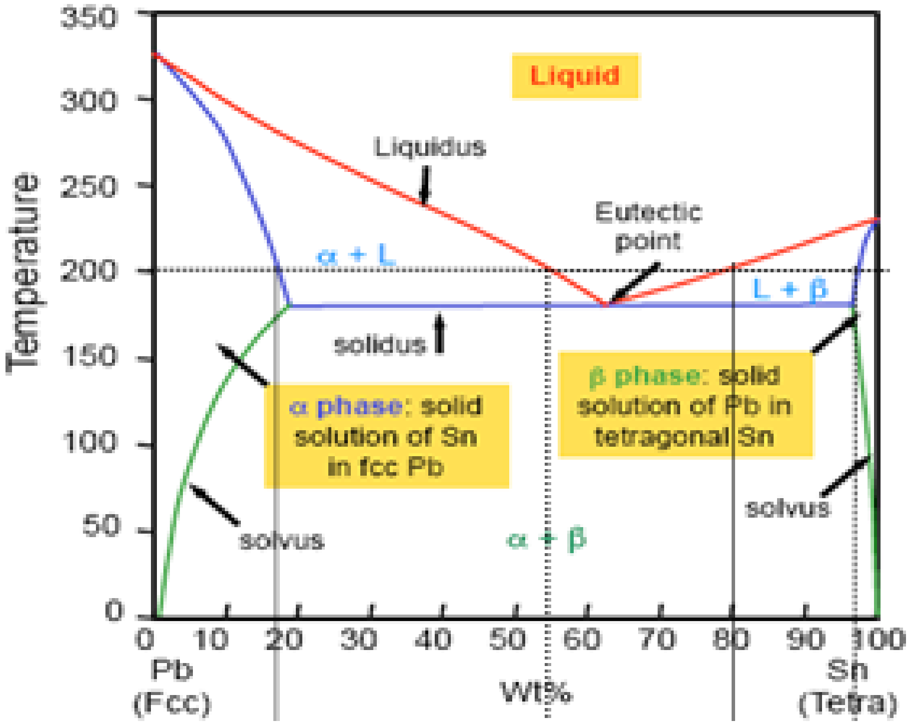
< Chapter 2 >

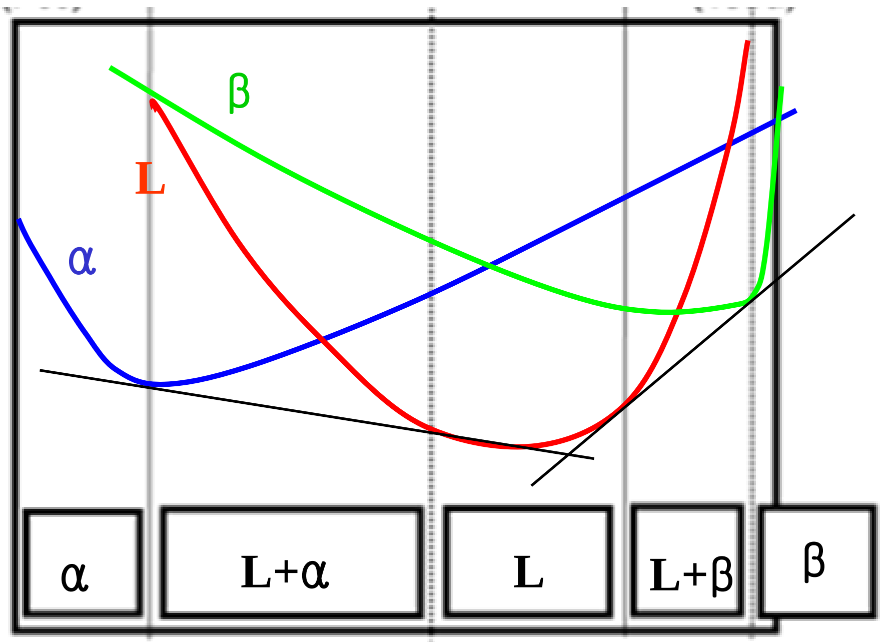
- **Diffusion**

- **Interstitial Diffusion – Fick's First Law**

- **Effect of Temperature on Diffusivity**

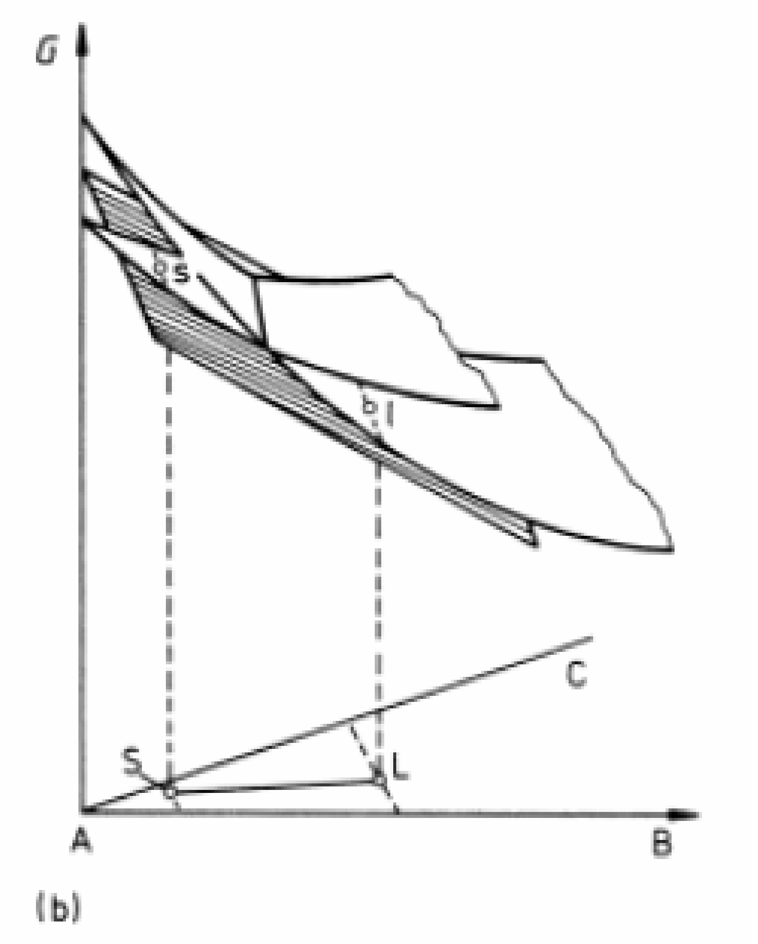
Tie line: binary system

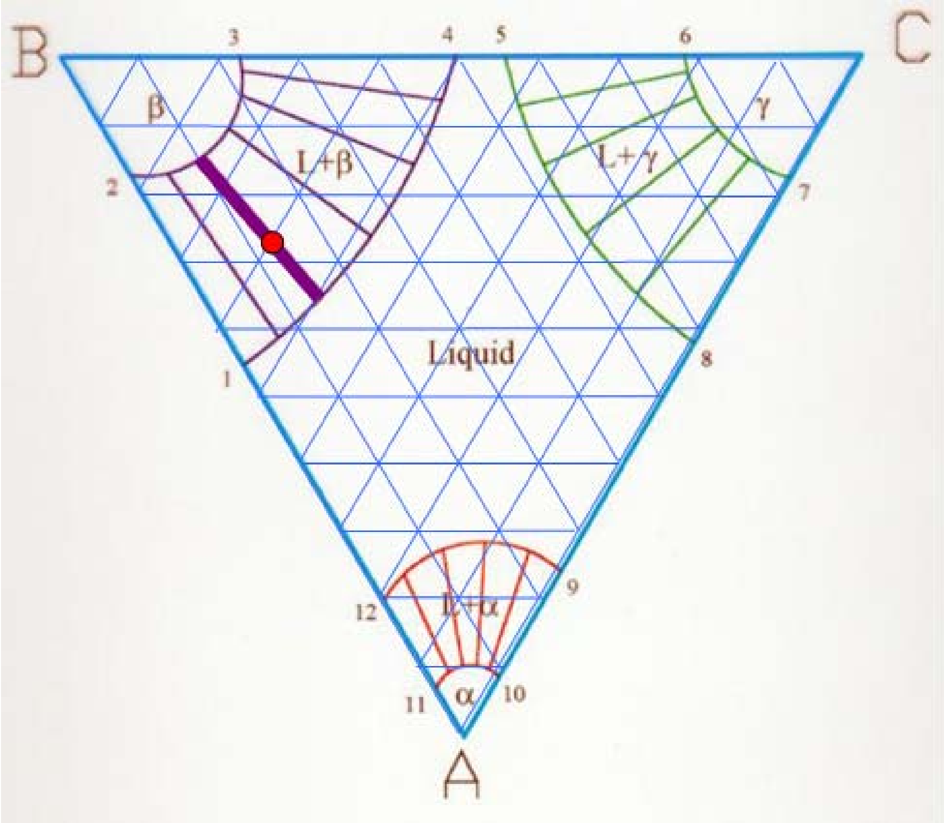




*** Simple Eutectic Systems** $\Delta H_{mix}^{L} = 0 \quad \Delta H_{mix}^{S} >> 0$

Tie line: ternary system





Diffusion

Diffusion

Diffusion : Mechanism by which matter transported through matter

What is the driving force for diffusion?

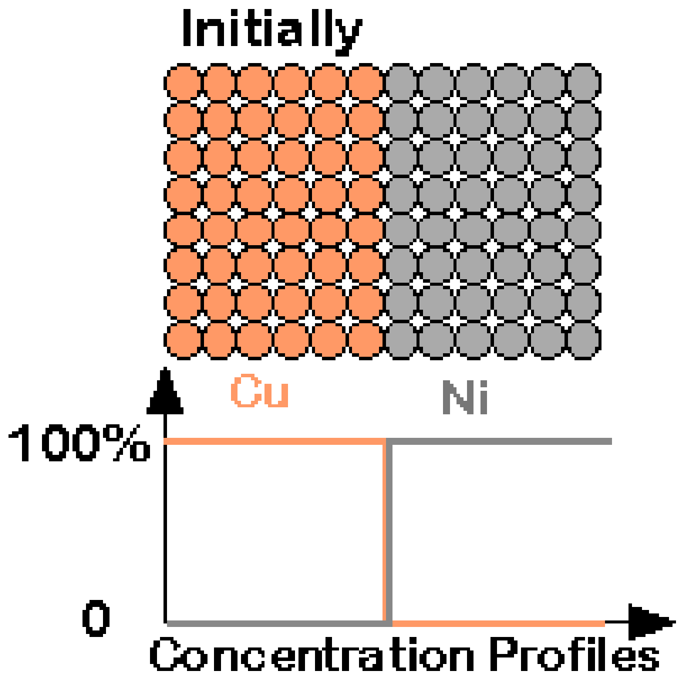
⇒ a concentration gradient (x)

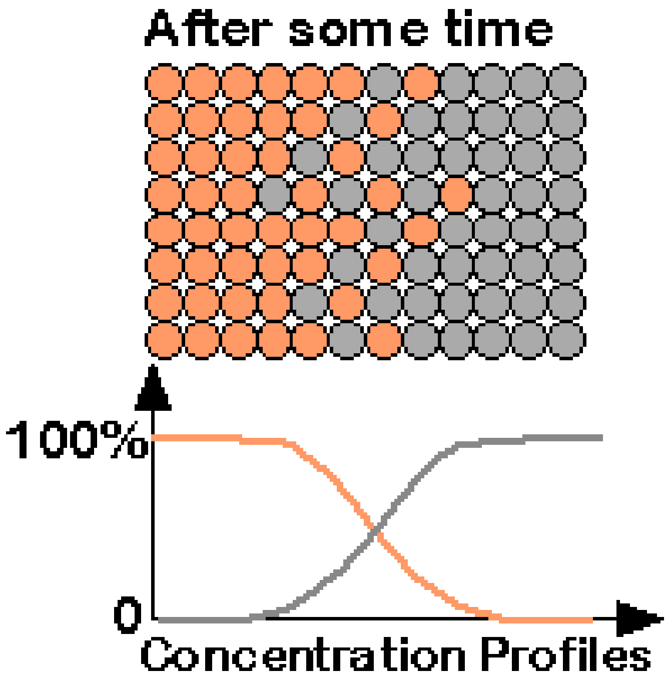
⇒ a chemical potential (o)

But this chapter will explain with concentration gradients for a convenience.

Diffusion: THE PHENOMENON

• Interdiffusion: in a solid with more than one type of element (an alloy), atoms tend to migrate from regions of large concentration.

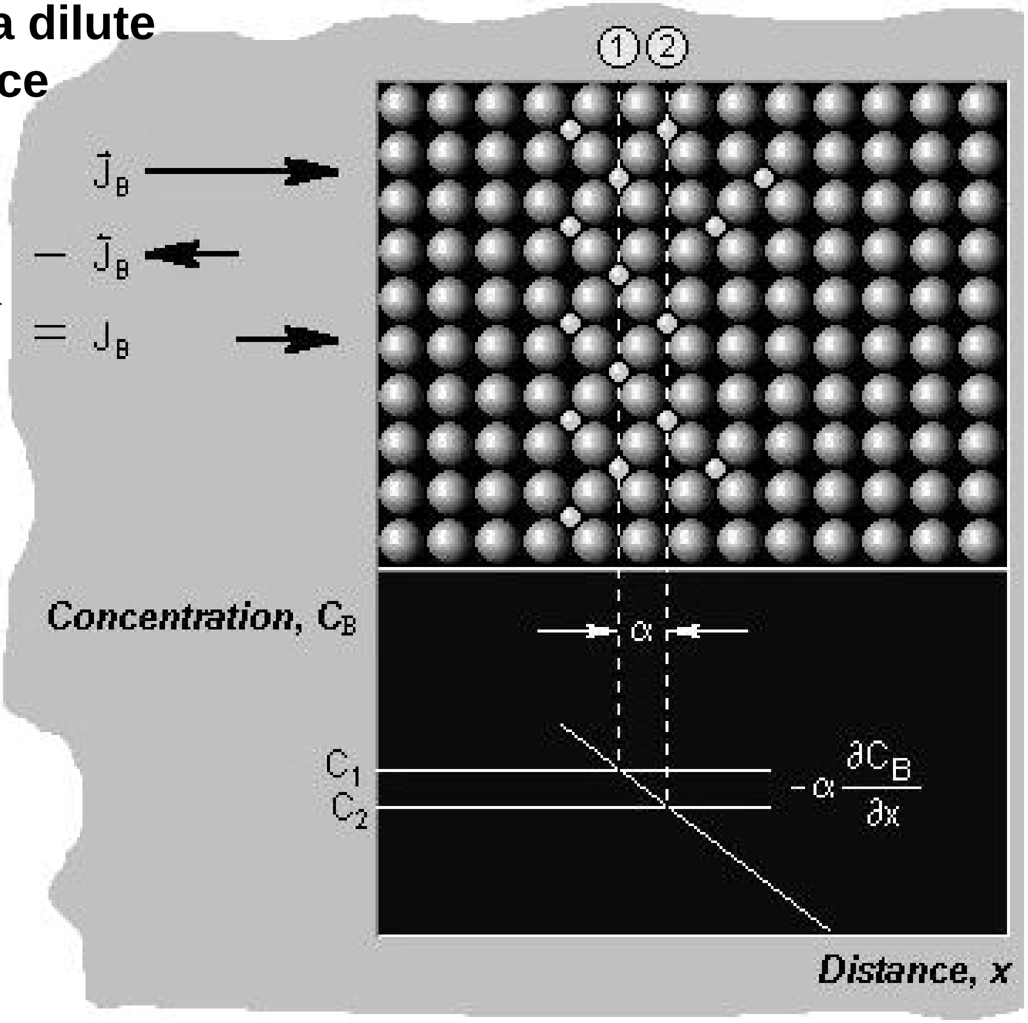




Substitutional diffusion **Interstitial diffusion**

Interstitial diffusion

Random jump of solute B atoms in a dilute solid solution of a simple cubic lattice



Assume that there is no lattice distortion and also that there are always six vacant sites around the diffusion atom.

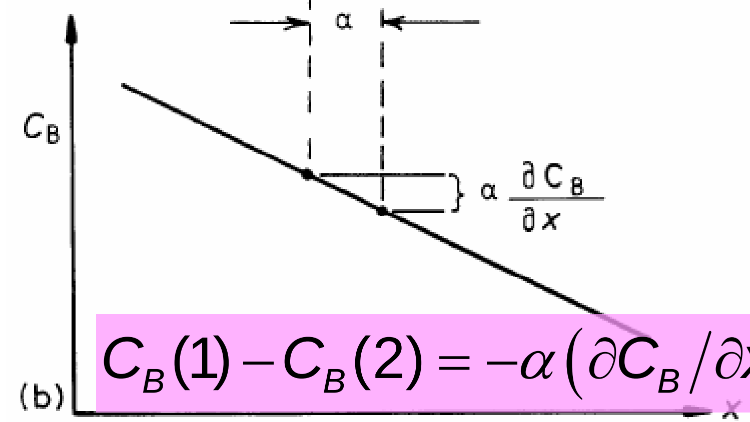
$$\boxed{J_B = \frac{1}{6}\Gamma_B n_1 - \frac{1}{6}\Gamma_B n_2}$$

J_B : Flux of B atom
Γ_B : Average jump rate of B atoms
n_1 : # of atoms per unit area of plane 1
n_2 : # of atoms per unit area of plane 2

Fick's First Law of Diffusion

$$J_B = \frac{1}{6}\Gamma_B n_1 - \frac{1}{6}\Gamma_B n_2 = \frac{1}{6}\Gamma_B (n_1 - n_2)$$

α: Jump distance



$$C_B(1) = n_1/\alpha\,,\ C_B(2) = n_2/\alpha$$

$$(n_1 - n_2) = \alpha\left(C_B(1) - C_B(2)\right)$$

$$C_B(1) - C_B(2) = -\alpha\left(\partial C_B/\partial x\right)$$

$$J_B = \frac{1}{6}\Gamma_B (n_1 - n_2) = -\left(\frac{1}{6}\Gamma_B \alpha^2\right)\frac{\partial C_B}{\partial x} = \boxed{-D_B \frac{\partial C_B}{\partial x}}$$

(atoms m^{-2} s^{-1})

➡ **Concentration varies with position.**

D_B: Intrinsic diffusivity or
Diffusion coefficient of B
⇒ depends on microstructure of materials

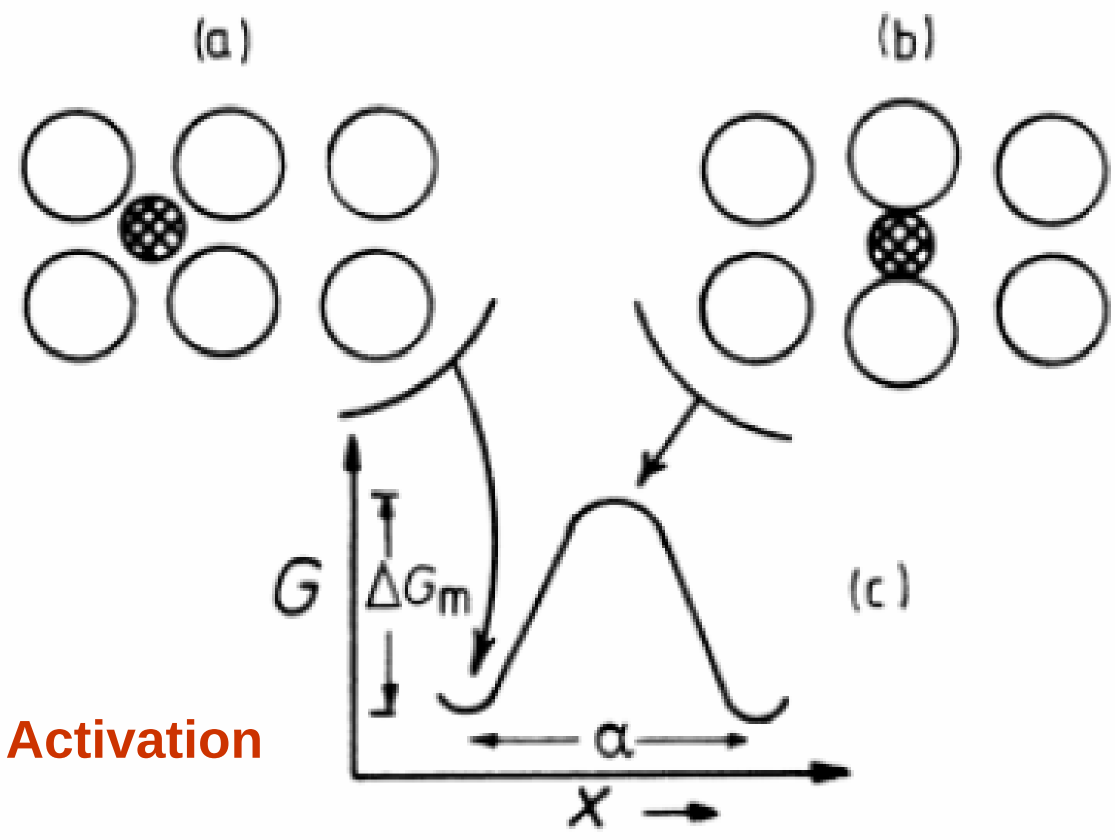
Magnitude of D in various media

Gas : D ≈ 10^{-1} cm^2/s
Liquid : D ≈ 10^{-4} ~ 10^{-5} cm^2/s
Solid : Materials near melting temp. D ≈ 10^{-8} cm^2/s
Elemental semiconductor (Si, Ge) D ≈ 10^{-12} cm^2/s

EFFECT OF TEMPERATURE on Diffusivity

Temperature ➡ Γ ➡ **D, Diffusivity**

(Interstitial atom jumps times per second)



Thermal Activation

Thermally activated process

jump frequency Γ_B ?

$$\Gamma_B = Z\nu \exp\left(-\Delta G_m / RT\right)$$

Z : **nearest neighbor sites**

ν : **vibration frequency**

ΔG_m : **activation energy for moving**

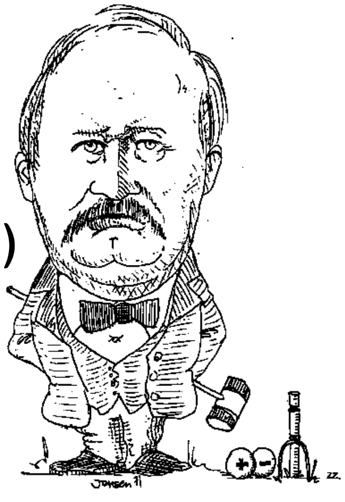
$$\left\{ \Delta G_m = \Delta H_m - T\Delta S_m \ , \ D_B = \frac{1}{6}\Gamma_B \alpha^2 \right\}$$

$$D_B = \left[\frac{1}{6}\alpha^2 Z\nu \exp\left(\Delta S_m / R\right)\right] \exp\left(-\Delta H_m / RT\right)$$

$$\Delta H_m \equiv Q_{ID}$$

$$\boxed{D_B = D_{B0} \exp \frac{-Q_{ID}}{RT}}$$

(Arrhenius-type equation)



Temperature Dependence of Diffusion

$$D_B = D_{B0} \exp \frac{-Q_{ID}}{RT}$$

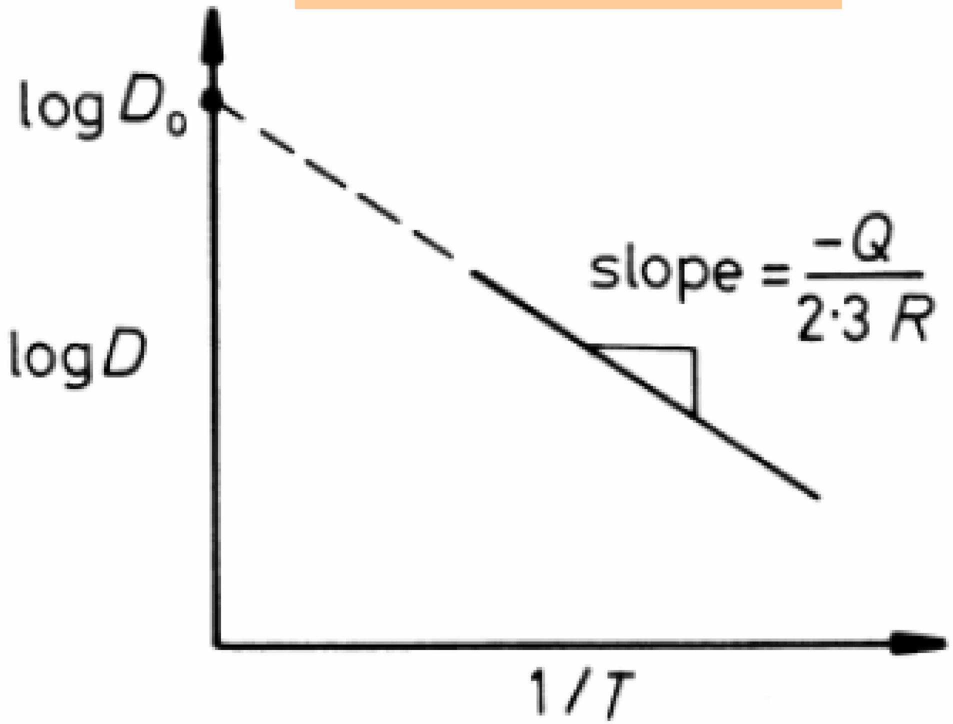


Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

How to determine Q_{ID} experimentally?

$$\log D = \log D_0 - \frac{Q}{2.3R}\left(\frac{1}{T}\right)$$

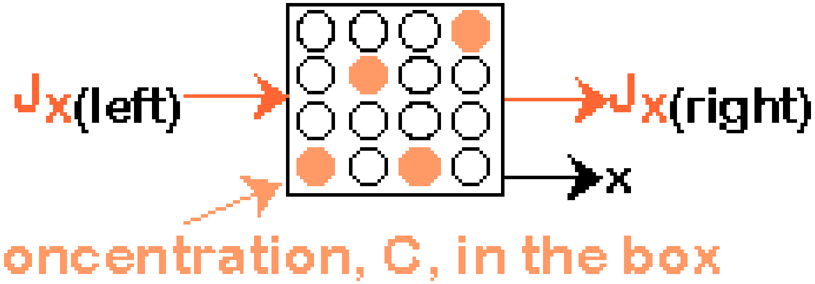
Therefore, from the slope of the D-curve in an log D vs 1/T coordinate, the activation energy may be found.

Contents for today's class

- Steady-state diffustion – Fick's First Law
- Nonsteady-state diffusion – Fick's Second Law
- Solutions to the diffusion Equations

Steady-state diffusion

The simplest type of diffusion to deal with is when the concentration at every point does not change with time.



Steady State:

$J_{x(left)} = J_{x(right)}$

- Apply Fick's First Law:

$$J_x = -D\frac{dC}{dx}$$

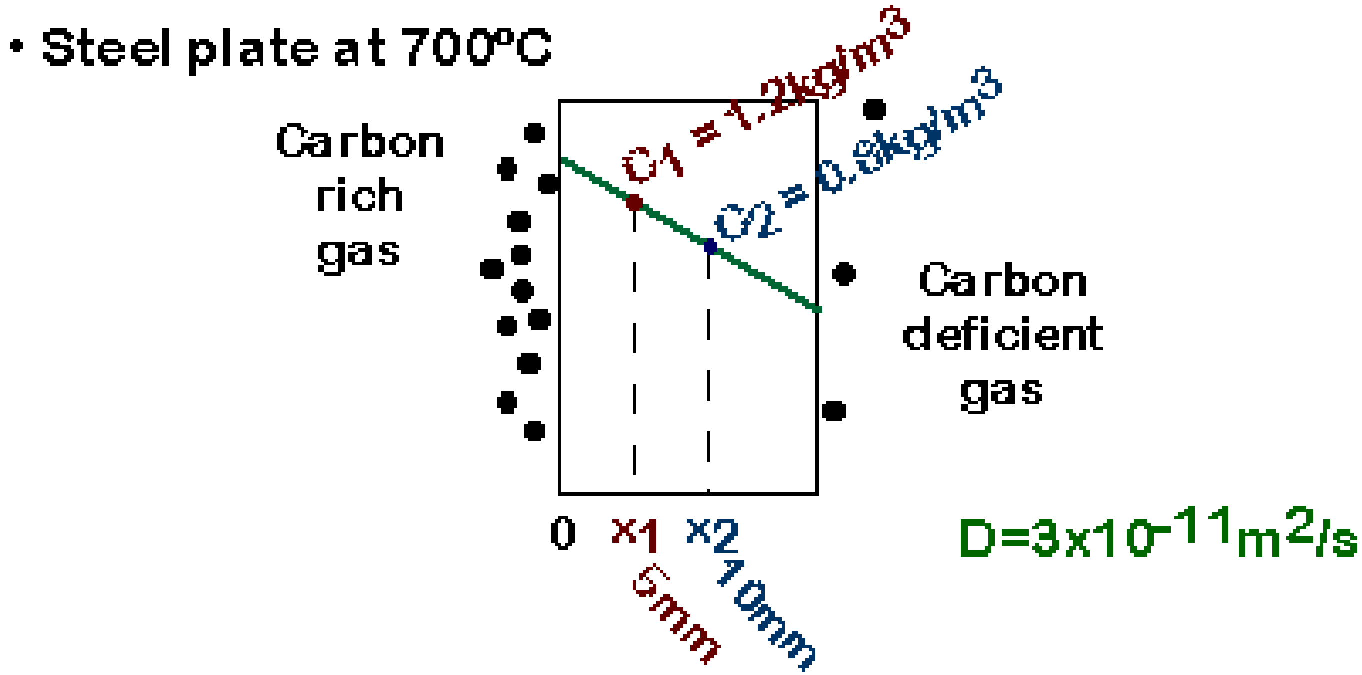
If $J_{x(left)} = J_{x(right)}$, then

$$\left.\frac{dC}{dx}\right|_{(left)} = \left.\frac{dC}{dx}\right|_{(right)}$$

$\Rightarrow$ the slope, dC/dx, is constant (does not vary with position)!

Steady-state diffusion

The simplest type of diffusion to deal with is when the concentration at every point does not change with time.



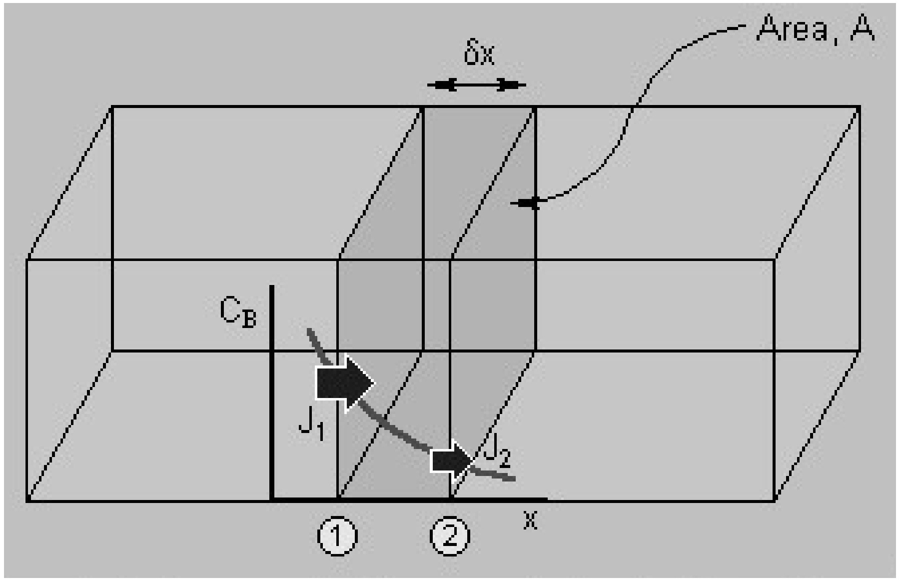
Q: How much carbon is transferring from the rich to deficient side?

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9}\ \frac{\text{kg}}{\text{m}^2\text{s}}$$

Nonsteady-state diffusion

In most practical situations steady-state conditions are not established, i.e. concentration varies with both distance and time, and Fick's 1st law can no longer be used.

How do we know the variation of C_B with time? → Fick's 2nd law



The number of interstitial B atoms that diffuse into the slice across plane (1) in a small time interval dt :

→ $J_1 A\, dt$ Likewise : $J_2 A\, dt$

Sine $J_2 < J_1$, the concentration of B within the slice will have increased by

Due to mass conservation

$$(J_1 - J_2) A \delta t = \delta C_B A \delta x \qquad \delta C_B = \frac{(J_1 - J_2) A \delta t}{A \delta x}$$

Nonsteady-state diffusion

$$J_2 = J_1 + \frac{\partial J}{\partial x}\delta x$$ (δx is small)

as δt => 0 $$\boxed{\frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}}$$

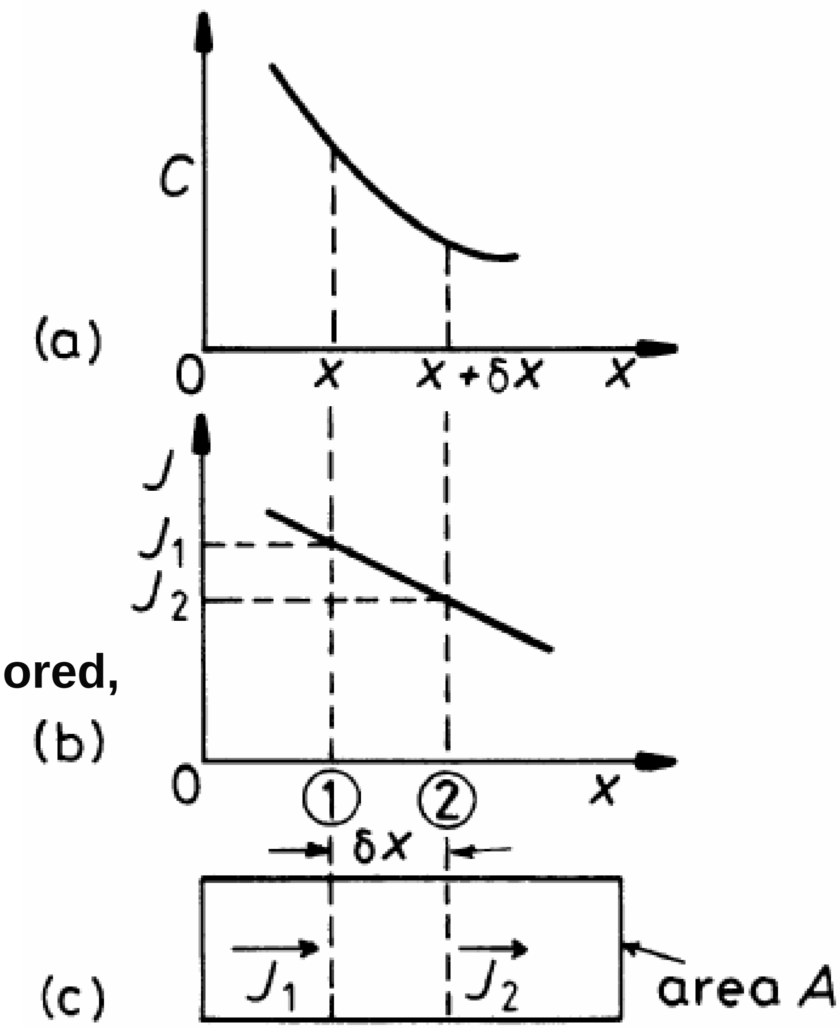
substituting Fick's 1st law gives

$$J_B = -D\frac{\partial C_B}{\partial x} \qquad \frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left(D_B \frac{\partial C_B}{\partial x}\right)$$

If variation of D with concentration can be ignored,

$$\boxed{\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}}$$

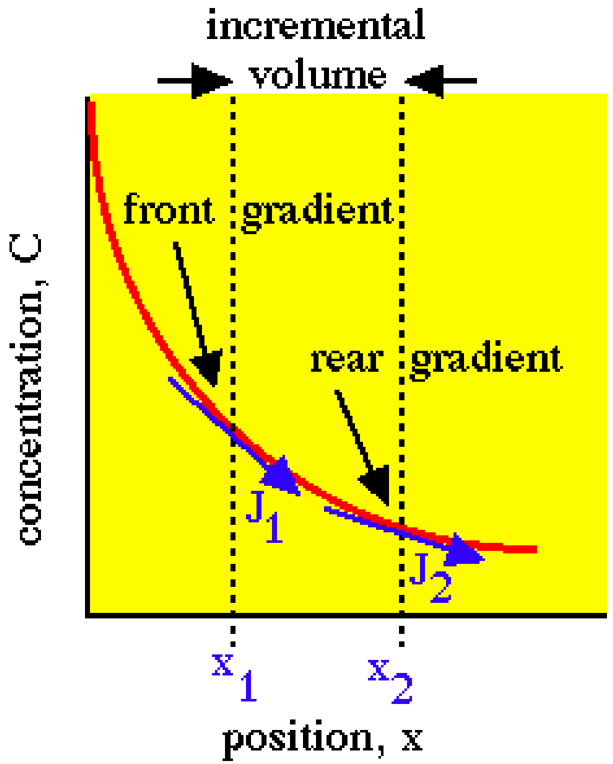
Fick's Second Law



Fick's Second Law

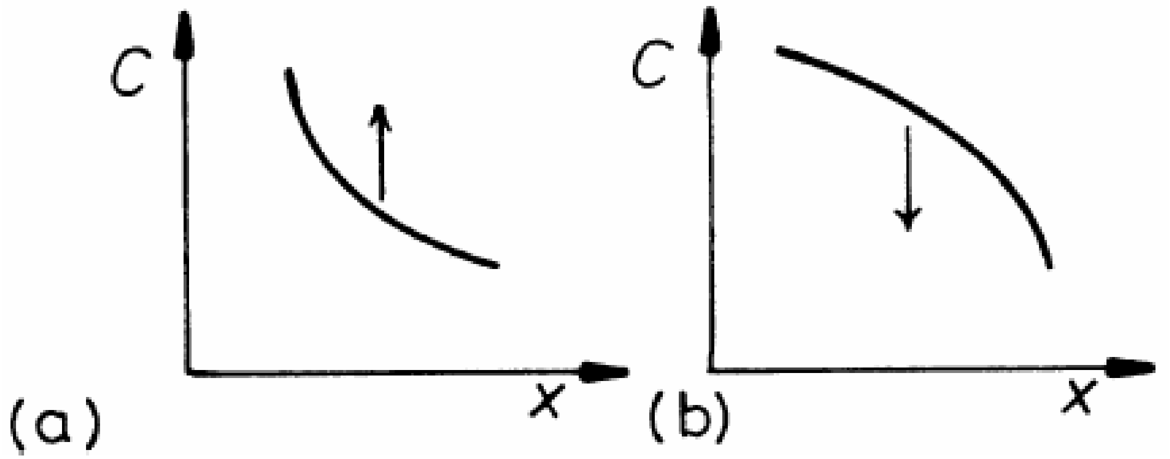
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

Concentration varies with time and position.



$$\frac{\partial^2 C_B}{\partial x^2} = ?$$

Note that $\frac{\partial^2 C_B}{\partial x^2}$ is the curvature.



Diffusion

Solutions to the diffusion equations

Ex1. Homogenization

of sinusoidal varying composition
in the elimination of segregation in casting

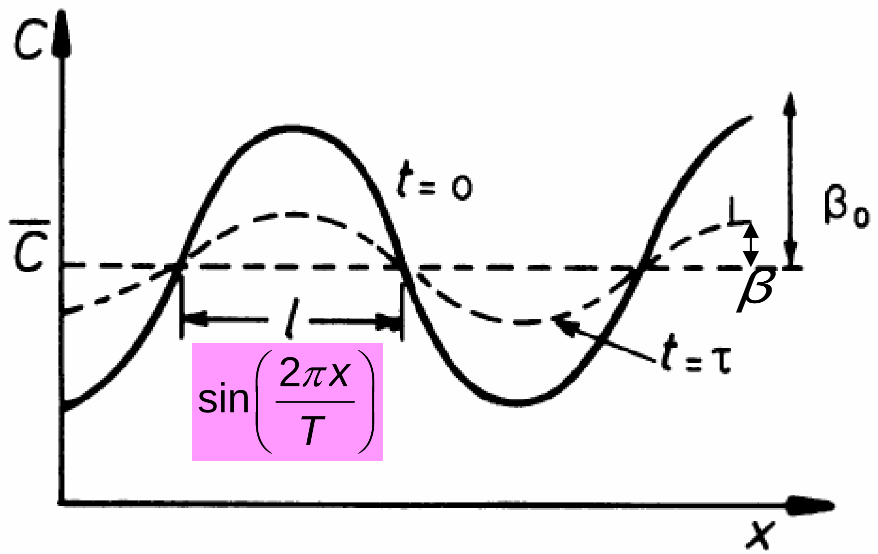


Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

Initial or Boundary Cond.?

$$C = \overline{C} + \beta_0 \sin\frac{\pi x}{l} \quad \textbf{at t=0}$$

$$\boxed{C = \overline{C} + \beta_0 \sin\frac{\pi x}{l} \exp\left(\frac{-t}{\tau}\right)}$$

$$\tau = \frac{l^2}{\pi^2 D} \qquad \tau : \text{relaxation time}$$

$$\beta = \beta_0 \exp(-t/\tau) \quad at \quad x = \frac{l}{2}$$

$\overline{C}$: the mean composition   ***l*** **: half wavelength**

β_0 : the amplitude of the initial concentration profile

Rigorous solution of $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$ for $C(x,0) = \overline{C} + \beta_0 \sin\frac{\pi x}{l}$

변수분리법이용

Let $C = XT$

$$X\frac{dT}{dt} = DT\frac{d^2X}{dx^2}$$

$$\frac{1}{DT}\frac{dT}{dt} = \frac{1}{X}\frac{d^2X}{dx^2} \equiv -\lambda^2$$

$$\frac{1}{T}\frac{dT}{dt} = -\lambda^2 D$$

$$\frac{d\ln T}{dt} = -\lambda^2 D$$

$$T = T_0 e^{\lambda^2 Dt}$$

$$\frac{d^2X}{dx^2} + \lambda^2 X = 0$$

$$X = A'\cos\lambda x + B'\sin\lambda x$$

$$\boxed{X(x) \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l}}$$

$$\therefore C = (A\cos\lambda x + B\sin\lambda x)e^{-\lambda^2 Dt}$$

$$\therefore C = A_0 + \sum_{n=1}^{\infty}(A_n \sin\lambda_n x + B_n \cos\lambda_n x)$$

$$t = 0 \rightarrow C \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l}$$

$$; A_0 = \overline{C}, B_n = 0, A_1 = \beta_0$$

($A_n = 0$ for all others)

$$\therefore C \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l} e^{-\frac{t}{l^2/\pi^2 D}}$$

$$\boxed{C = \overline{C} + \beta_0 \sin\frac{\pi x}{l}\exp\left(\frac{-t}{\tau}\right)}$$

Solutions to the diffusion equations

Ex2. Carburization of Steel

The aim of carburization is to increase the carbon concentration in the surface layers of a steel product in order to achiever a harder wear-resistant surface.

1. **Holding the steel in CH_4 and/or Co at an austenitic temperature.**
2. **By controlling gases the concentration of C at the surface of the steel can be maintained at a suitable constant value.**
3. **At te same time carbon continually diffuses from the surface into the steel.**

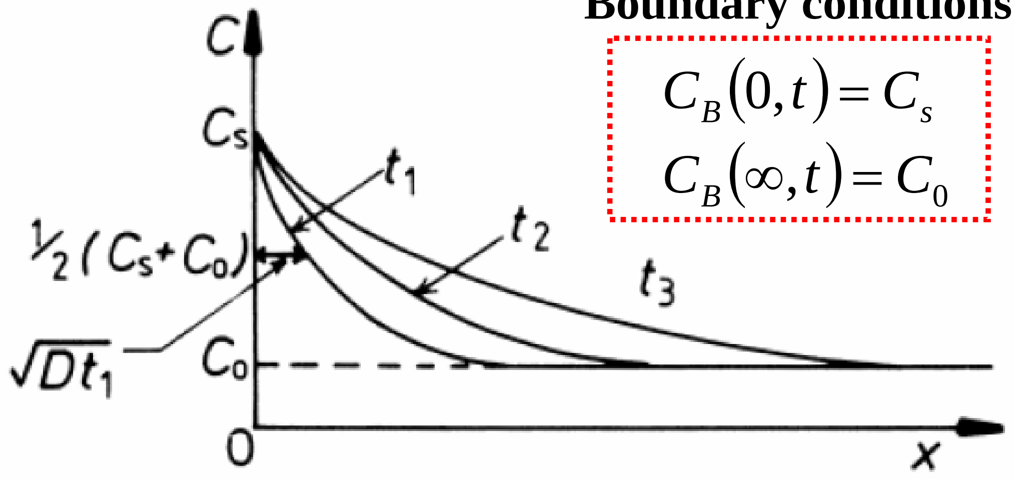
Carburizing of steel

Depth of Carburization?

The error function solution:

$$C = C_s - (C_s - C_0)\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$erf(Z) = \frac{2}{\sqrt{\pi}}\int_0^Z e^{-y^2}dy$$



Boundary conditions

$$\boxed{\begin{aligned} C_B(0,t) &= C_s \\ C_B(\infty,t) &= C_0 \end{aligned}}$$

Fif. 2.11 Concentration profiles at successive times ($t_3 > t_2 > t_1$) for diffusion into a semi-infinite bar when the surface concentration C_s is maintained constant.

$$\frac{C_s - C}{C_s - C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

erf(0.5)≈0.5

$$C = \frac{C_s + C_0}{2}$$

- Since erf(0.5)≈0.5 the depth at which the carbon concentration is midway between C_s and C_0 is given $(x/2\sqrt{Dt}) \cong 0.5$

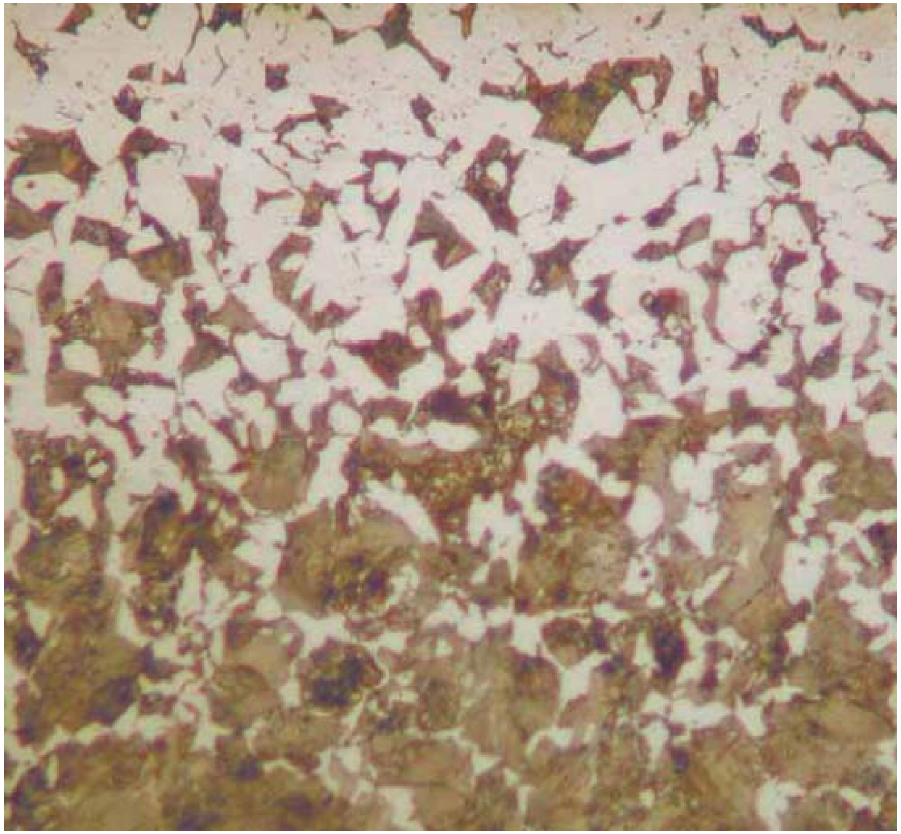
that is $x \cong \sqrt{Dt}$ → **Depth of Carburization**

Carburizing of steel

Thus the thickness of the carburized layer is $\cong \sqrt{Dt}$.
Note also that the depth of any isoconcentration line is directly proportion to $\sqrt{Dt}$, i.e. *to obtain a twofold increase in penetration requires a fourfold increase in time.*

Decarburization of Steel?

$$\boxed{C = C_0 erf\left(\frac{x}{2\sqrt{Dt}}\right)}$$



Error function

In mathematics, the error function (also called the Gauss error function) is a non-elementary function which occurs in probability, statistics and partial differential equations.

It is defined as:

$$\boxed{\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt.}$$

By expanding the right-hand side in a Taylor series and integrating, one can express it in the form

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)n!} = \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3} + \frac{x^5}{10} - \frac{x^7}{42} + \frac{x^9}{216} - \cdots \right)$$

for every real number x. **(From Wikipedia, the free encyclopedia)**

Error function

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2)\,dy$$

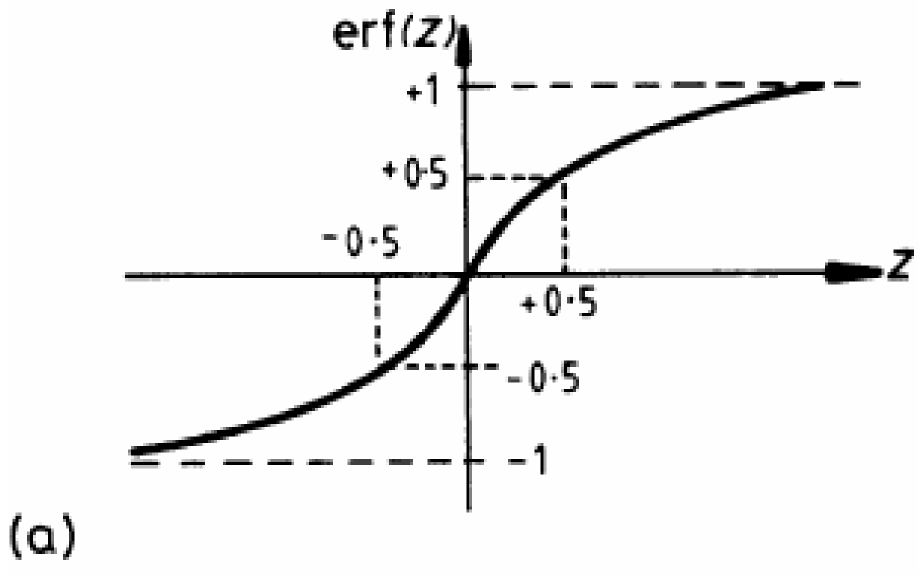


Fig. 2.12 (a) Schematic diagram illustrating the main features of the error function.

Table 1-1. The Error Function

z	erf(z)	z	erf(z)
0	0	0.85	0.7707
0.025	0.0282	0.90	0.7969
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

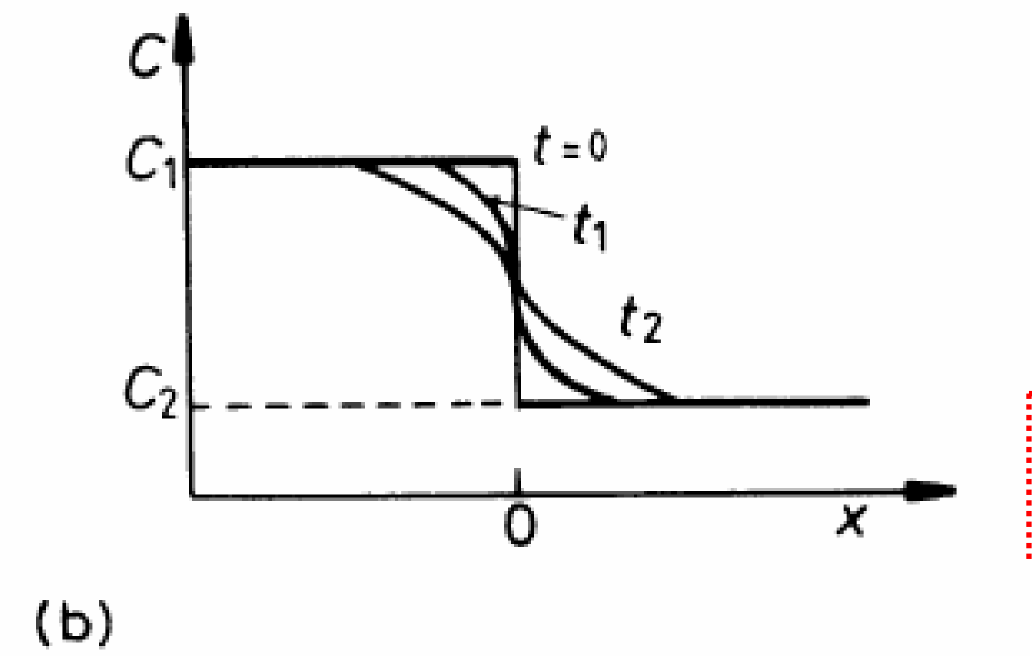
Solutions to the diffusion equations

Ex3. Diffusion Couple

Joining of two semi-infinite specimens of compositions C_1 and C_2 ($C_1 > C_2$)

Draw C vs. x with time t = 0 and t > 0.

Boundary conditions?



$$C = C_1 \quad t = 0, \; -\infty < x < 0$$
$$C = C_2 \quad t = 0, \; 0 < x < \infty$$
$$C = C_1 \quad x = -\infty, \; 0 < t < \infty$$
$$C = C_2 \quad x = \infty, \; 0 < t < \infty$$

$$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Fig. 2.12 (b) Concentration profiles at successive times ($t_2 > t_1 > 0$) when two semi-infinite bars of different composition are annealed after welding.

The section is completed with 4 example solutions to Fick's 2nd law: *carburisation*, *decarburisation*, *diffusion across a couple* and *homogenisation*.

The solutions given are as follows:

Process	**Solution**
Carburisation	$C = C_S - (C_S - C_0)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_S = Surface concentration C_0 = Initial bulk concentration
Decarburisation	$C = C_0\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_0 = Initial bulk concentration
Diffusion Couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_1 = Concentration of steel 1 C_2 = Concentration of steel 2
Homogenisation	$C = C_{mean} + \beta_0 \sin\left(\frac{\pi x}{\lambda}\right)\exp\left(-\frac{t}{\tau}\right)$ C_{mean} = Mean concentration b_0 = Initial concentration amplitude l = half-wavelength of cells t = relaxation time